

Research Article

Reactions of *o,o'*-Dihydroxy Azo Dyes with the Third Group M(III) Ions: A Spectroscopic and Electrochemical Study

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The reactions of some metal ions of the third group (M(III)) with azo dyes were studied. Attention was focused on azo dyes with two hydroxy groups in *ortho*-positions to azo group: eriochrome red B (ERB), eriochrome black T (EBT), eriochrome blue SE (EBSE), calcon (Calc), and kalces (KLC). The chelation is responsible for interaction of these dyes with Al(III), Sc(III), rare earth elements (REE) ions, Ga(III), and In(III). The complexes were studied using vis- and IR-spectrometry. One irreversible peak (P1) of complexes reduction was observed on voltammograms for all studied metal ions. The second peak P2 was observed only for Ga complexes with all investigated azo dyes. Based on the study, the possible mechanism of complexes reduction was proposed. Linear behavior has been found between the reduction peak currents of a set of metal complexes and the concentration of the respective metal cations. This can be used for metal ions determination by voltammetric methods.

1. Introduction

Azo dyes belong to the one of the largest class of analytical reagents. Their important feature is electroactivity, which makes them very important reagents for the voltammetric determination of metal ions [1–3], especially nonelectroactive metals.

It is known that the electrochemical behaviour of Al(III), Sc(III), Ga(III), and REE(III) is not straightforward [4–8]. The reduction potentials of these metal ions are more negative than -1.2 V on mercury electrodes. Therefore, direct voltammetric methods for Al(III), Sc(III), Ga(III), and REE(III) determination are limited by a concurrent reduction of hydrogen ion. Another possibility is indirect analysis based on the formation of complexes of M(III) with reducible organic reagents, such as azo dyes. The resulting complex produces a discrete reduction peak which is well separated from the peak of free dyes and measured current of complex reduction is sensitive to M(III) concentration.

In our previous papers, the complexes of some M(III) ions with ERB, EBT, EBSE, Calc, and KLC were studied [9–12]. Methods developed were utilized for voltammetric determination of REE, In, and Sc in model solutions, alloys, and scintillation materials with the limit of quantitation in range 10^{-7} – 10^{-6} M. The observed different reduction behavior of studied complexes leads us to investigate peculiarities of M(III) interaction with azo dyes—ERB, EBT, EBSE, Calc, and KLC. Their structures are shown in Figure 1.

2. Experimental

2.1. Apparatus. A potentiostat ПИИ-50-1.1 (Russia) connected to a personal computer was used for electrolysis and cyclic voltammetric measurements. Linear sweep voltammetric measurements were carried out utilizing certified home-made digital device equipped with personal computer and temperature-controlled three-electrode cell, volume 10 mL.

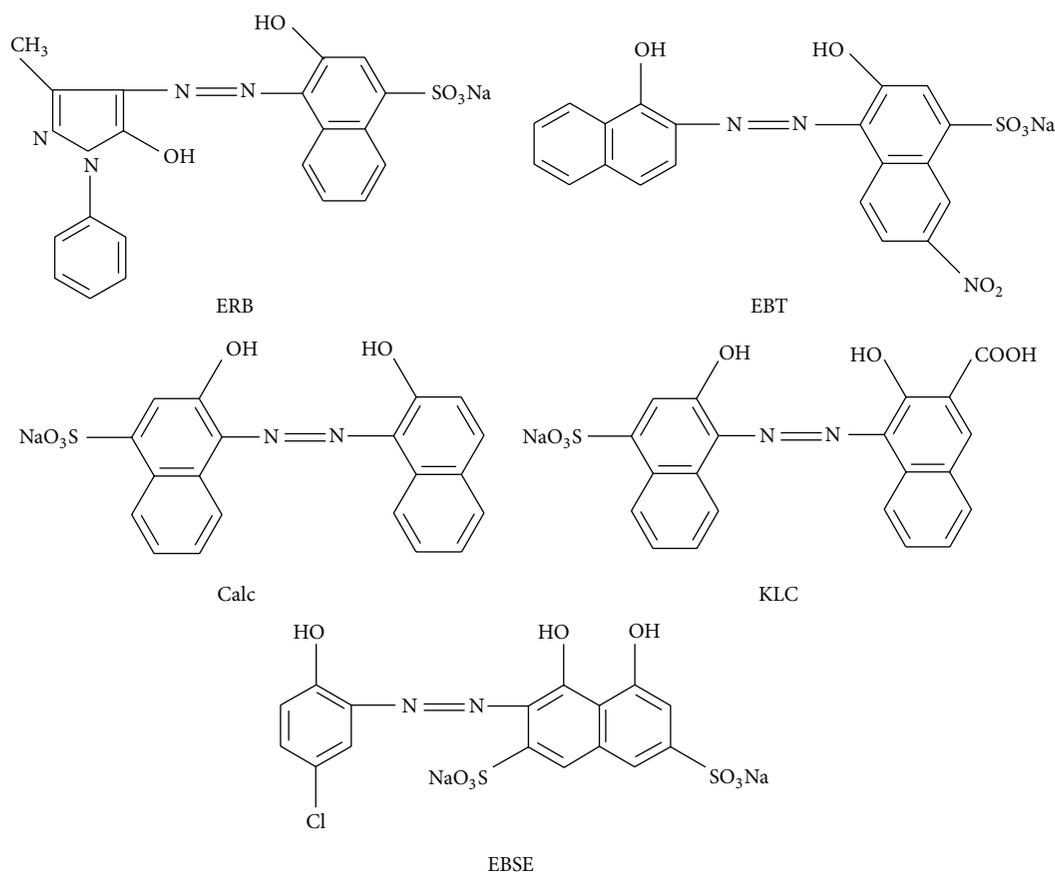


FIGURE 1: Formula of azo dyes.

A dropping mercury electrode with a drop time of 10.8 s at an open circuit served as working electrode. A saturated calomel electrode and platinum wire electrode were used as the reference and auxiliary electrodes, respectively.

Electronic absorption spectra were recorded using HACH DR/4000 V spectrophotometer and cuvette with $l = 1$ cm. IR spectra (in KBr) were recorded on Shimadzu 8700, SR ATR spectrometer.

The pH of solution was measured potentiometrically using MV 870 DIGITAL-pH-MESSERÄT pH-meter.

2.2. Reagents. All solutions were prepared from double distilled water. Stock solutions (10^{-2} M) of Sc, Ga, In, and REE were prepared by dissolving the appropriate quantity of pure metal containing 99.999% of the major substance in a mixture of conc. HCl and conc. HNO₃ (Sfera sim (Ukraine), cp grade). The metal's solutions were standardized using complexometry. Stock solutions (10^{-3} M) of ERB (Chemapol), EBT (Реахим (Russia)), EBSE (Acros organics), Calc (BDH), and KLC (POCH S.A. (Poland)) were prepared by dissolving the given amount of reagents in aqua-ethanol mixture (where ethanol content was 40% for ERB, 50% for EBT, 25% for EBSE, and 10% for Calc and KLC). These solutions were standardized spectrophotometrically. The following supporting electrolytes were employed: acetic acid, sodium hydroxide,

ammonia, and ammonium chloride (Sfera Sim (Ukraine), cp grade).

2.3. Procedure. Working solutions for spectrophotometric and voltammetric investigations were prepared by adding reagents to the volumetric flask in the following order: acetic (pH 3.5–6.0), acetic-ammonium (pH 6.0–8.0) or ammonium (pH 8.0–10.5) buffer solution, azo dye solution, solution of M(III), and filled by double distilled water up to the mark. The obtained solutions were stirred and poured into the cuvette or voltammetric cell. Before obtaining, the voltammograms solutions were purged with argon for 10 min.

Samples of complex compounds to record IR spectra were prepared by mixing of azo dye solution (10^{-2} M) and M(III) ion solution (10^{-2} M) in ratio 1:1. The optimal pH was maintained by ammonia solution. The obtained solutions of complexes were dried at room temperature.

3. Results and Discussion

3.1. Spectroscopic Studies

3.1.1. Vis-Spectra. The vis-spectra of azo dyes (EBT, EBSE, Calc, and KLC) exhibit intense bands at 510–560 nm and 470 nm (ERB). The vis-spectra of azo dye–M(III)–complexes are very similar to those of free dyes (Figure 2, Table 1),

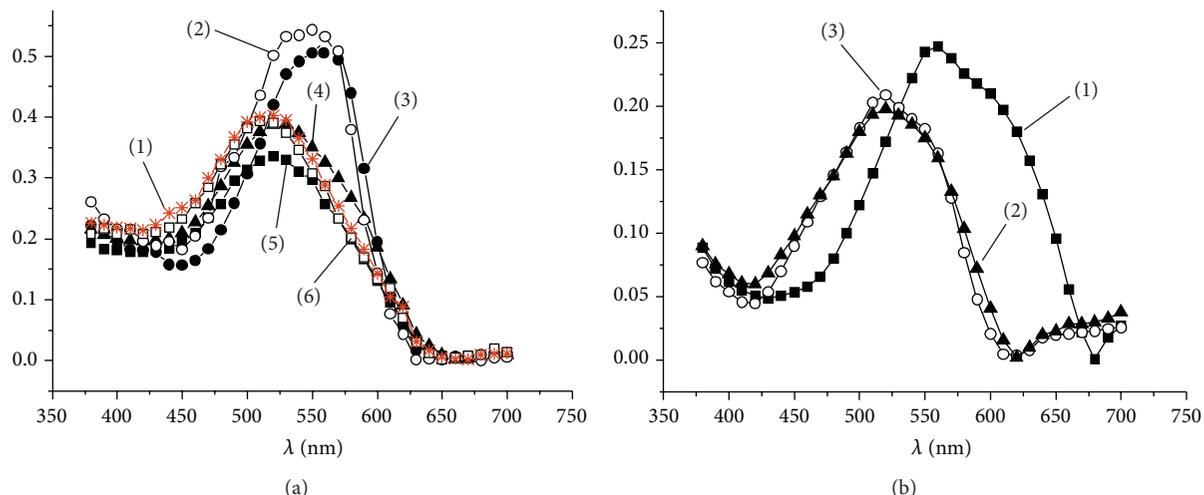


FIGURE 2: (a) Absorption spectra of $4 \cdot 10^{-5}$ M Calc (1) with $4 \cdot 10^{-5}$ M of Al(III) (2), Ga(III) (3), In(III) (4), Sc(III) (5), and Y(III) (6); pH 4.9. (b) Absorption spectra of $4 \cdot 10^{-5}$ M KLC (1) with $4 \cdot 10^{-5}$ M of Sc(III) (2) and Y(III) (3); pH 9.5.

while a 10–30 nm bathochromic shift of absorption maxima was observed. This effect can be caused by the displacement of the naphthalic hydrogens during chelation process. It is known that deprotonation of phenols is accompanied by a bathochromic shift of absorption band and increasing of absorbance [13]. Figure 3 shows spectra obtained for H_2L^- , HL^{2-} , and L^{3-} forms of Calc. Spectrum of Ga(III) complex is similar to that of HL^{2-} form, but the absorption band is 10 nm hypsochromic shifted in comparison with that for HL^{2-} . This observation cannot be explained by the simple removal of naphthalic hydrogens. In addition, oxygen of ligand gives its lone pair to gallium during chelation.

In the case of Sc(III) or Y(III) with KLC complexes, hypsochromic shift of absorption maxima in their spectra was observed in comparison with the spectra of free reagent (Figure 2). Sc(III) and Y(III) interact with azo dye at pH 9.5. KLC exists at this medium predominantly in HL^{3-} form ($pK_3 = 8.8\text{--}9.4$ [14]). Metal ions displace the second naphthalic hydrogen in dye's molecule forming L^{4-} . For *o,o'*-dihydroxy azo dyes, it has been observed that removal of the first proton is accompanied by a bathochromic shift in the maximum of the visible absorption band, while partial conversion of the HL to L is accompanied by a slight hypsochromic effect [15]. Consequently, the absorption spectrum of Sc (or Y) with KLC may be interpreted as arising through the influence of the metals on the spectrum of L^{4-} .

Electronic spectra of Calc, KLC, and EBSE in the presence of In(III) ions do not show significant shift from those observed for free dyes. The maxima in spectra of free azo dye and azo dye—In(III)—are located in close vicinity (in the case of KLC and EBSE) or there is no shift observed (in the case of Calc). In some cases, those small shifts (Table 1) can be explained substantially by violation of optical transition, but not complex formation.

3.1.2. IR Spectra. IR spectra of free azo dyes and their complexes with M(III) ions have been obtained in the range

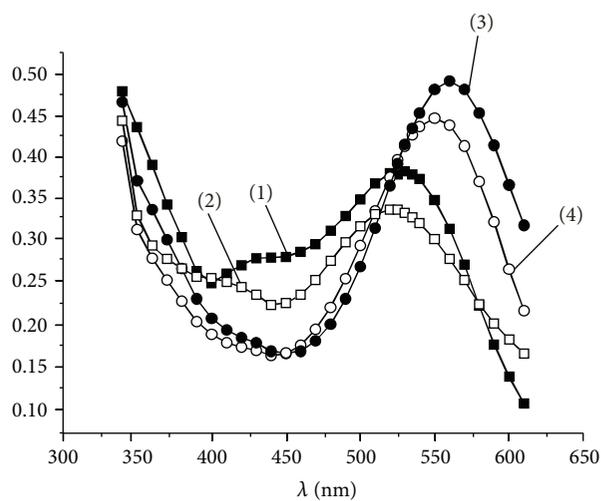


FIGURE 3: Absorption spectra of $4 \cdot 10^{-5}$ M Calc 1 in 1 M NaOH; 2 at pH 4.4; 3 at pH 9.5, and 4 with $4 \cdot 10^{-5}$ M of Ga(III) at pH 4.4.

of $550\text{--}4000\text{ cm}^{-1}$. Some of them are shown in Figures 4, 5, and 6. Also, Table 2 summarizes the IR peak positions and their assignments.

IR spectra of complexes are different from those of free dyes, but they are mostly similar to each other. Only registered differences were observed at 2000 cm^{-1} and 1750 cm^{-1} for Sc and In complexes, which are not recognised in azo dye's spectra or in spectra of Ga complexes. Also, a band at $3270\text{--}3300\text{ cm}^{-1}$ is present only in spectra of Ga complexes.

Before analysing the IR spectra of complexes, it is necessary to note some characteristic bands present in azo dyes, which are responsible for complexation. The important feature of azo compounds is the presence of a hydroxy group conjugated with (i.e., *ortho* or *para* to) the azo group, which is responsible for their tautomerism [24]. Azo dyes can exist

TABLE I: Spectroscopic characteristics of M(III)-azo dye systems.

Metal	pH	$\lambda_{H,L}^{\max}$, nm	$\lambda_{M(H,L)q}^{\max}$, nm	$\Delta\lambda$, nm	Changes of absorbance at λ^{\max}
Eriochrome red B					
Al	8.0	470	488	18	Decreased
Sc	8.0	470	496	26	Decreased [16]
Ga	4.5	465	500	35	Increased substantially
	8.0	470	502	32	Decreased [16]
In	8.0	470	494	24	Decreased [16]
Tm	8.0	470	484	14	Decreased [16]
Calcon					
Al	4.9	520	550	30	Increased
Sc	4.9	520	520	0	Decreased
Ga	4.9	520	550	30	Increased
In	4.9	520	520	0	Decreased
Y	4.9	520	510	0	Decreased
Kalces					
Al	5.5	550	570	20	Increased
Sc	9.5	560	520	40	Decreased
Ga	4.5	550	570	20	Increased
In	4.6	550	560	10	Decreased
Y	9.5	560	520	40	Decreased
Eriochrome black T					
Al	4.0	520	540	20	Increased
Sc	5.5	510	540	30	Increased substantially
Ga	4.5	520	550	30	Increased substantially
In	8.5	590	550	40	Decreased
Eriochrome blue SE					
Al	5.0	520	540	20	Increased
	8.0	530–560 (wide maximum)	530	—	Increased
Sc	6.1	530	550	20	Decreased
Ga	7.0	530	550	20	Decreased
In	4.4	520	530	10	Decreased
	7.0	530	550	20	No changes
Sm			540–550	—	
Nd	7.9	530–560 (wide maximum)	2 maxima at 530 and 550	—	Increased
Dy			530–550	—	

as hydroxyazo or keto-hydrazone tautomers [24, 25]. The predominant form is determined by their thermodynamic stability. IR spectroscopy is a suitable tool that can provide information about the presence of hydroxyazo or keto-hydrazone tautomer. The obtained results by IR spectroscopy indicate the existence of both tautomers of studied azo dyes—ERB, EBT, Calc, and KLC. The band at 1600 cm belongs to vibration of C=O group, which is in keto-hydrazone form of dye [18, 20, 25]. Also, the bands corresponding to the vibration of groups have been registered, which are present in hydroxyazo form. The bands at $\sim 1500\text{ cm}^{-1}$ and 1400 cm^{-1}

are caused by vibration of $-\text{N}=\text{N}-$ group in *cis*- and *trans*-isomers, respectively [17, 18, 21]. The bands assigned to $\nu(\text{O}-\text{H})$ and $\delta(\text{O}-\text{H})$ are registered at $3400\text{--}3550\text{ cm}^{-1}$, and $1150\text{--}1170\text{ cm}^{-1}$, respectively [13, 17, 18].

The recorded IR spectra of M(III)-HL indicate that ERB, EBT, Calc, and KLC in complex compounds are present as hydroxyazo tautomers. The band of C=O group vibration in spectra of complexes is very weak, whereas there is a strong band of $-\text{N}=\text{N}-$ vibration. Also, this band for *cis*-isomer is very weak, but for *trans*-isomer, it is stronger, than in free dyes. Thus, the ligand in complexes is predominantly

TABLE 2: Peak assignments for IR spectra (values given in cm^{-1})^a.

H_nL (ERB, EBT, Calc, and KLC)	$M(H_xL)_q$	Assignment	Reference
3400–3550, m, br	3400–3550, w (absorbance decreases)	$\nu(\text{O-H}), \nu(\text{N-H})$	[13, 17, 18]
Absent	3270–3300 (registered only in Ga complex)	Not assigned	
Absent	3110–3150, m (registered in all M complexes)	Not assigned	
3050, w	3050, m	Aromatic $\nu(\text{C-H})$	[19]
3070, w (for EBT)	3030, m (for In-ERB)		
2920, 2845, w (for ERB)		Asym., sym. $\nu(\text{C-H})$ of methyl group	[17]
1680, s (for KLC)	Absent in Ga and Sc complexes	$\nu(\text{COOH})$	[13]
1600, m	1600, w	$\nu(\text{C=O}), \nu(>\text{C=N})$ in hydrazone tautomer; aromatic $\nu(\text{C=C})$	[18, 20]
1500–1510, m	1500, w (M-ERB; Sc, Ga-Calc, Ga-KLC) absent in M-EBT, Sc-KLC	$\nu(\text{N=N})$ in <i>cis</i> -isomer	[17, 18, 21]
1400, m	1390–1410, s	$\nu(\text{N=N})$ in <i>trans</i> -isomer	[17, 18, 21]
1350, s (for EBT)	1350–1360, s	$\nu(\text{NO}_2)$	[13, 17, 21, 22]
1200–1280, m	1200–1280, w	$\nu(\text{-C-O})$ in azo tautomer, $\nu(\text{Ar-N})$ in hydrazone tautomer	[18]
1150–1170, s	Absent in Ga complexes 1150–1170, w in Sc, In complexes	$\delta(\text{O-H})$	[18]
1100–1140, s	Absent in Ga-HL complexes 1100–1140, w in Sc, In complexes	$\nu(\text{-C-N=})$	[18, 21, 22]
1025–1050, s	1050–1075, s for Ga complex 1050, m for Sc, In complexes	$\nu(\text{N=N})$	[23]

^as: strong; m: medium; w: weak; br: broad.

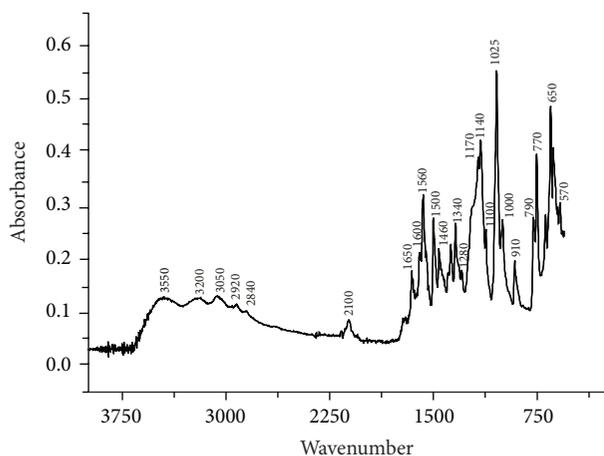


FIGURE 4: IR spectrum of ERB.

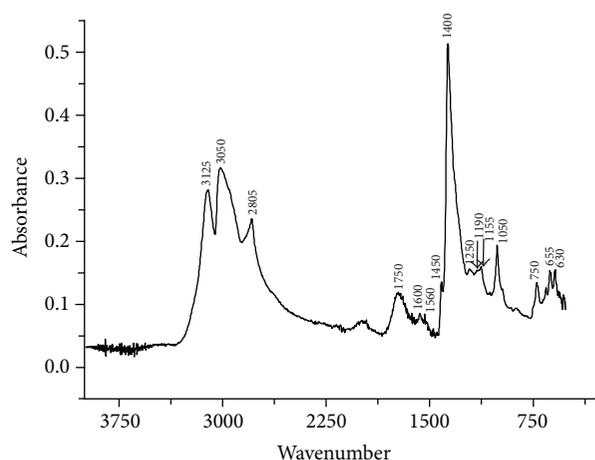


FIGURE 5: IR spectrum of ERB-Sc(III).

as *trans*-isomer. The strong $\nu(\text{N=N})$ band of free ligand at $1025\text{--}1050\text{ cm}^{-1}$ has been shifted to $1050\text{--}1075\text{ cm}^{-1}$ on coordination in the complexes.

However, $\nu(\text{O-H})$, $\delta(\text{O-H})$, and $\nu(\text{C-O})$ bands are very weak or even absent in spectra of complexes. This may be explained by the substitution of hydrogen ions by M(III)

during complexation and formation of O–M bond, instead of absence of azo form of ligand.

The changes in IR spectra of complexes compared to free azo dye indicate that complexation is carried out through O–H and N=N groups of hydroxyazo form of ligands. This is in agreement with previously published data about interaction of other metal ions with o,o'-dihydroxy azo dyes [24–27].

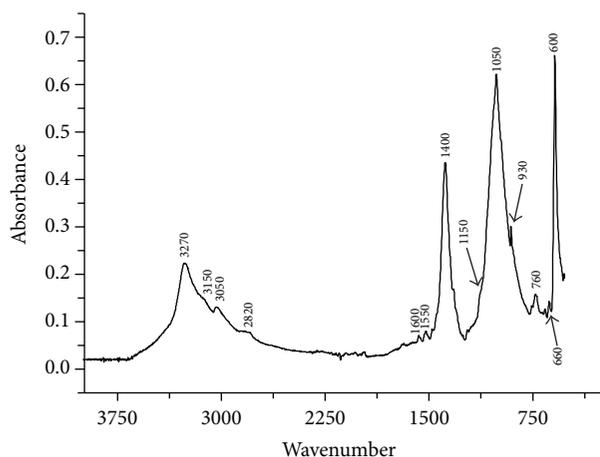
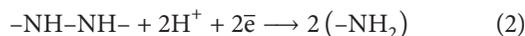
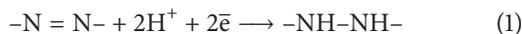


FIGURE 6: IR spectrum of ERB-Ga(III).

3.2. Electrochemical Studies. The cyclic voltammograms of investigated azo dyes exhibited one to three irreversible cathodic peaks [9, 10]. The number of peaks depends on pH and nature of compounds. The peaks observed are due to the reduction of azo $-N=N-$ center. The reduction mechanism includes the formation of hydrazo derivatives followed by the cleavage of the $-N=N-$ bond and the final formation of amines [28, 29], according to the following:



3.2.1. Reduction of Al(III), Sc(III), and REE(III) Complexes with Azo Dyes. In the presence of Al(III), Sc(III), and REE(III) ions, a new peak (P1) is observed at more cathodic potentials (Figure 7), related to the reduction of the ligand involved in the complexation. The authors of [28] explained the potential shift by the involvement of the azo group in complexation, with a consequent stabilization of the nitrogen electrons in the ring, which made it less available to reduction. The reduction of complexes (peak P1) is an irreversible process as is demonstrated by the absence of anodic peaks on polarograms. The peak potentials are pH-dependent. The potentials are shifted to more negative values with pH increases. This indicates the involvement of protons in the rate-determining step during reduction processes of complexes, which is in agreement with the mechanism of free azo dye reduction according to schemes (1) and (2). The response (I , μA) from complexes is adsorption-controlled:

- (1) cathodic peaks are symmetric;
- (2) the slope of a log-log plot of peak current versus scan rate was higher than 0.5 indicating the adsorption-controlled response [30].

The area of new peak depends linearly on metal concentration, which allows us to use it for quantitative determination of Al(III), Sc(III), or REE(III).

The electrolysis was used in order to obtain relevant information on the reactants. The solution containing equal

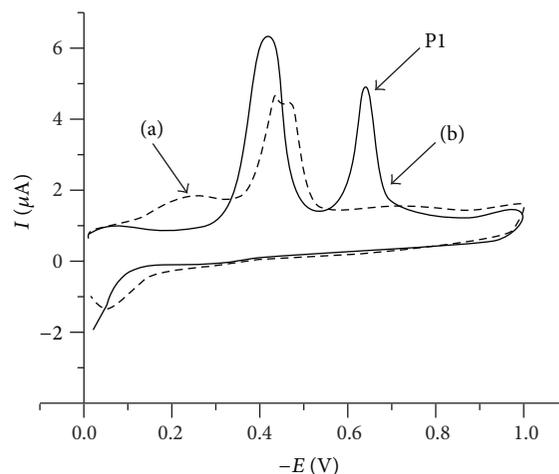


FIGURE 7: Voltammograms of $4 \cdot 10^{-5}$ M EBT (a) and in the presence of $4 \cdot 10^{-5}$ M Sc(III) (b); pH 5.5, $\nu = 0.5 \text{ V} \cdot \text{s}^{-1}$.

amounts ($2 \cdot 10^{-5}$ M) of M(III) and azo dye at $\text{pH}_{\text{optimal}}$ underwent the electrolysis during 5 hours. An electrolysis potential was ~ 0.02 – 0.03 V more negative than the peak potential of complex. After the peaks current of azo dye and complex had significantly decreased, the colourless solution was obtained. The decolorization was caused by the breakage of conjugated chain, which contains N atoms of azo group. Also no peak on the polarogram was observed (Figure 8). This means that the free azo dye and complex have been reduced and are absent. If a definite amount of M(III) was added to the cell, the peak P1 corresponding to the reduction of complex was not obtained. If a definite amount of appropriate azo dye was added to the solution, the peaks corresponding to the reduction of free azo dye and complex were obtained again (Figure 8). The metal ions, which did not undergo reduction, formed complex with added azo dye and peak P1 was observed on polarogram. The above mentioned experiment has confirmed that ligand is responsible for electrode reaction.

3.2.2. Reduction of Ga(III) Complexes with Azo Dyes. The electrochemical behaviour of Ga-azo dye complexes is different from that of Al, Sc, and REE complexes. In the presence of Ga(III) ions, two new peaks appear at more cathodic potentials (Figure 9). The occurrence of less cathodic new peak (P1) is caused by the reduction of ligand involved in complexation, as in the case of Al, Sc, and REE complexes with studied azo dyes. This was also confirmed by the electrolysis (Figure 8).

The more cathodic new peaks (P2) are registered at potentials, which are nearly the same for all Ga complexes with the investigated azo dyes. The potentials do not depend on pH. This means that peak P2 cannot be caused by the reduction of azo dye as ligand because if azo dye is the reactant, protons will be consumed and E_{P2} will become more negative when pH is higher.

The electrochemical reduction of Ga(III) complexes is an irreversible process since $I_c/I_a > 1.0$ and $\Delta E_p = E_{p,a} - E_{p,c}$

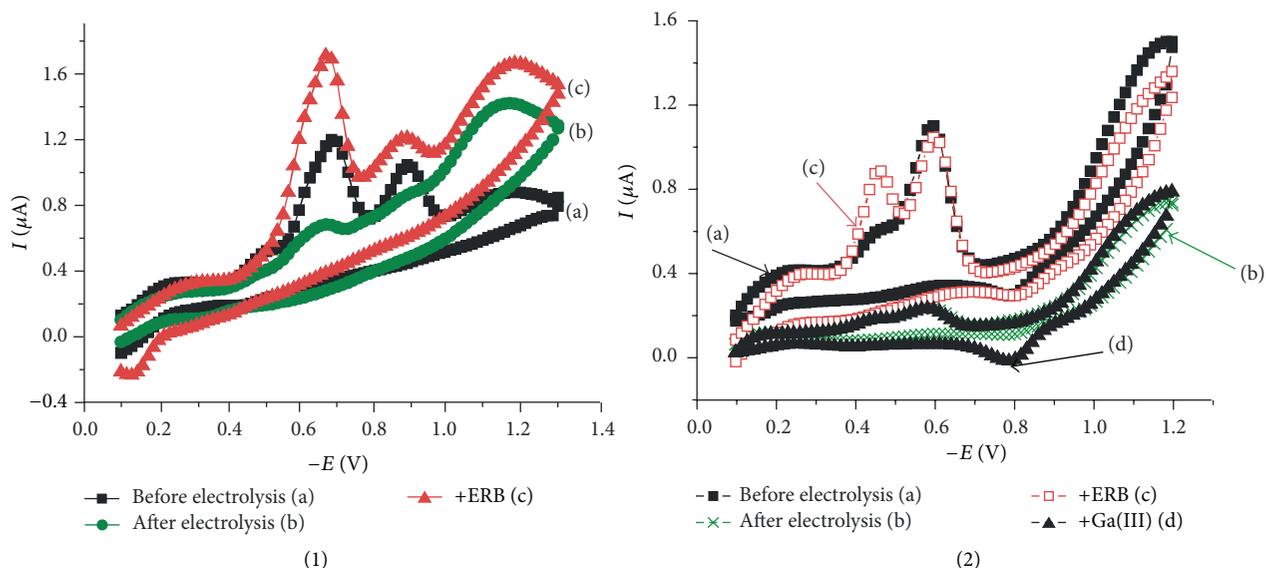


FIGURE 8: Voltammograms of Sc(III)-ERB (1), pH 8.0, and Ga(III)-ERB (2), pH 4.6: before electrolysis (a), after electrolysis (b), + ERB (c), and + Ga(III) (d), $C_{\text{M(III)}} = C_{\text{ERB}} = 2 \cdot 10^{-5}$ M.

was higher than 0.059/3. A log-log plot of peak P2 current versus scan rate at pH 4.0–5.4 for ERB, 4.5 for EBT, 5.9 for Calc, and 4.5–5.6 for KLC provides a slope equal to 0.5. At pH 3.6 for ERB and KLC, 4.0 for EBT, and 4.7 for Calc, the slope was in the range of 0.3–0.4.

From the literature data, it is known that Ga(III) is reduced to Ga(0) in $\text{Ga}(\text{Sal})_3$ complex at $E_{1/2} = -0.988$ V, where Sal is salicylate ion. In this case, the process was irreversible [6]. Also, it has been reported about $\text{Ga(III)} \rightarrow \text{Ga(0)}$ wave in the presence of NH_4SCN at $E_{1/2} = -0.85$ V or pyrocatechol at $E_{1/2} = -1.0$ V [6] and peak in the presence of morin at $E_p = -0.95$ V [31]. In all these cases, the waves were caused by the reduction of Ga(III) to Ga(0). The electrochemical reduction of Ga(III) ions from these complexes is a catalytic process. The adsorbed ligands play a role of catalysts. The catalytic effect of ligand can be explained in the following way. Adsorbed ligand in complexes is linked to Hg electrode and at the same time it is bound with metal ion. The electron transfer from the cathode to metal ion through ligand occurs easier than directly from mercury cathode. Thus, Ga(III) ions from complex are reduced at less negative potentials ($E_{1/2} = -0.85$ – -1.00 V) than in the presence of indifferent electrolyte ($E_{1/2} = -1.36$ V– -1.60 V) [6, 32].

The potentials of peak P2 (Table 3) of investigated Ga(III) complexes with ERB, EBT, Calc, and KLC are in the same range as for the complexes discussed above. Thus, the appearance of peak P2 for Ga-azo dye complexes can be explained by the reduction of Ga(III) ions to Ga(0) in the complexes. In the electrochemical process ligands, azo dyes are catalysts. It is known that azo dyes can be readily adsorbed by mercury electrode. In adsorbed state, they facilitate the electron transfer from electrode to Ga(III) ions. Thus, the reduction of Ga(III) to Ga(0) at less cathodic potential ($E_p \sim -1.0$ V) than in the presence of noncomplexing electrolytes ($E_{1/2} = -1.36$ V– -1.60 V) [6] can be observed.

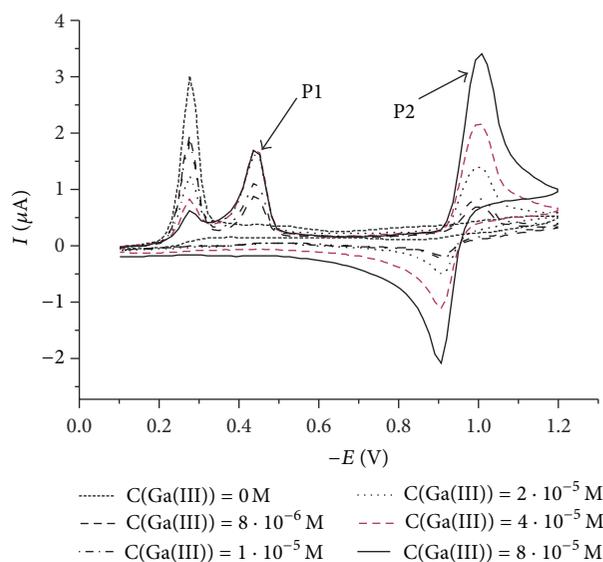


FIGURE 9: Voltammograms of $4 \cdot 10^{-5}$ M KLC and in the presence of $8 \cdot 10^{-6}$ M, $1 \cdot 10^{-5}$ M, $2 \cdot 10^{-5}$ M, $4 \cdot 10^{-5}$ M, and $8 \cdot 10^{-5}$ M Ga(III); pH 4.5, $\nu = 0.5$ V \cdot s $^{-1}$.

Peaks P1 and P2 increase linearly with increasing of Ga(III) concentration allowing its determination.

3.2.3. Reduction of In(III) Complexes with Azo Dyes. The similar behavior was observed for reduction of ERB and EBT in the presence of In(III) ions as for Al(III), Sc(III), and REE(III) complexes with these dyes. A new peak is formed by the reduction of ligand from complex of ERB-In or EBT-In.

TABLE 3: Voltammetric characteristics of M(III)-azo dye system.

Azo dye	Metal	pH for investigation (pH _{optimal} ^a)	New peaks	$-E_p^{\text{complex}}$, V (at pH _{optimal})	Linear range, M
ERB	Sc	8.0–8.6	One peak P1	0.89	$8 \cdot 10^{-7} - 2 \cdot 10^{-5}$
	Ga	3.3–4.6	Two peaks P1, P2	0.50–0.61	$1 \cdot 10^{-7} - 1 \cdot 10^{-5}$ (P1)
		4.0–4.6		0.96–1.01	
	In	7.7–8.2	One peak P1	0.83	$4.0 \cdot 10^{-7} - 1.5 \cdot 10^{-5}$
	REE	9.5	One peak P1	0.84 [11]	
		10.0	One peak P1	0.96 [9]	$4 \cdot 10^{-7} - 2 \cdot 10^{-5}$
EBT	Al	5.0	One peak P1	0.51	It was not studied
	Sc	5.5–6.5	One peak P1	0.64	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$
	Ga	4.1–4.5	Two peaks P1, P2	0.40–0.44	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$ (P1)
		4.4–4.5		0.95	
	In	8.3–8.7	One peak P1	0.66	It was not studied
	REE	8.0–8.2	One peak P1	0.70	$1 \cdot 10^{-6} - 1 \cdot 10^{-5}$
		10.5	One peak P1	0.80 [10]	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$
KLC	Al	5.1	One peak P1	0.52	$8 \cdot 10^{-7} - 2 \cdot 10^{-5}$
	Sc	4.8	One peak P1	0.59	$6 \cdot 10^{-7} - 1 \cdot 10^{-5}$
		8.2–9.0		0.73–0.77	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$
	Ga	3.9–5.2	Two peaks P1, P2	0.42–0.46	$2 \cdot 10^{-7} - 2 \cdot 10^{-5}$ (P1)
		4.4–5.5		0.98–0.99	$4 \cdot 10^{-7} - 1 \cdot 10^{-5}$ (P2)
	In	5.0–6.0	No new peaks observed, increasing of the current of $\text{In}^{3+} \rightarrow \text{In}^0$ peak		$1 \cdot 10^{-6} - 1 \cdot 10^{-4}$
	REE	9.0–9.5	One peak P1	0.89	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$
Calc	Sc	3.5	One peak P1	0.53	$2 \cdot 10^{-6} - 4 \cdot 10^{-5}$
	Ga	3.7–4.5	Two peaks P1, P2	0.45–0.49	$1 \cdot 10^{-7} - 1 \cdot 10^{-5}$ (P1)
		4.3–5.3		0.98–1.04	
	In	4.0–5.5	No new peaks observed, increasing of the current of $\text{In}^{3+} \rightarrow \text{In}^0$ peak		$1 \cdot 10^{-6} - 1 \cdot 10^{-4}$
	REE		No new peaks observed		—
EBSE	Al	6.6–7.3	One peak P1	0.67–0.69	$6 \cdot 10^{-7} - 1 \cdot 10^{-5}$
	Sc	6.4–7.0	One peak P1	0.76–0.77	$1 \cdot 10^{-7} - 1 \cdot 10^{-5}$
		8.2–9.2		0.77–0.79	$8 \cdot 10^{-7} - 1 \cdot 10^{-5}$
	Ga	5.4–7.0	Two peaks P1, P2 (the peak is not clear)	0.52–0.59	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$
	In	4.9–5.6	No new peaks observed, increasing of the current of $\text{In}^{3+} \rightarrow \text{In}^0$ peak	0.61	$2 \cdot 10^{-6} - 2 \cdot 10^{-5}$
		6.7–8.9	One new peak (not observed in the absence of EBSE)	0.63–0.67	$6 \cdot 10^{-7} - 2 \cdot 10^{-5}$
	REE	7.5–8.5	One peak P1	0.80	$1 \cdot 10^{-6} - 2 \cdot 10^{-5}$

^aRange of pH at which current of complex peak is maximal or constant.

On the other hand, the electrochemical behaviour of KLC, Calc, or EBSE in the presence of In(III) is different. The current of $\text{In}^{3+} \rightarrow \text{In}^0$ reduction increases with addition of KLC, Calc, or EBSE to In(III) solution (Figure 10). This effect can be explained by changes in double electrical layer in the presence of organic reagent. It is known that electron transfer rate is determined by effective potential jump between electrode and the center of electroactive particle. Obviously,

adsorption of azo dye's anion on DME causes an increase of effective potential jump between positively charged mercury electrode and the centre of electroactive particle of In^{3+} . Consequently, this leads to an increase of electrode process rate where In^{3+} ions are involved. An increase of current of metal ion reduction in the presence of adsorbed compounds on the electrode is called the "bridge effect" [32]. A similar effect was described in [33].

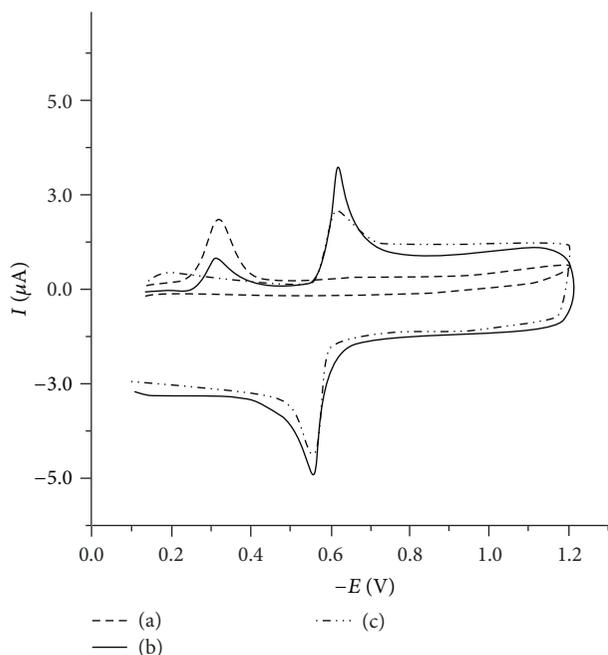


FIGURE 10: Voltammograms of EBSE (a), In(III)-EBSE (b), and In(III) (c); $C_{\text{EBSE}} = C_{\text{In(III)}} = 4 \cdot 10^{-5}$ M; pH 5.0, $\nu = 0.5 \text{ V} \cdot \text{s}^{-1}$.

4. Conclusions

Sc(III), Ga(III), In(III), and REE(III) ions react with ERB, EBT, EBSE, Calc, and KLC forming complex compounds. The changes in vis- and IR spectra of studied azo dyes indicate that oxygen in OH-group and nitrogen in N=N-group are responsible for chelation with metal ions. The cyclic voltammetry has been used for the determination of complexes' electrochemical properties. It was determined that complexes of Sc, Ga, REE with studied azo dyes, and In with ERB and EBT were reducible and new analytical signals (peaks) appeared on the voltammograms. The reduction process of complexes (peak P1) is irreversible and has adsorptive nature. The mechanism of complex conversion on the electrode involves the reduction of azo -N=N- centre from the ligand. Only Ga(III) complexes with azo dyes are characterized by additional peak (P2) of central ion reduction, which is catalyzed by the ligand-azo dye.

No new peaks were observed for In(III) in the presence of EBSE, Calc, and KLC. The peculiarity of In(III) reduction in the presence of these dyes is the increase of current of In(III) reduction to In(0) at low concentrations of dyes. The increasing of current resulted from the changes in the double electrical layer when the azo dyes' anions are adsorbed on the electrode.

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